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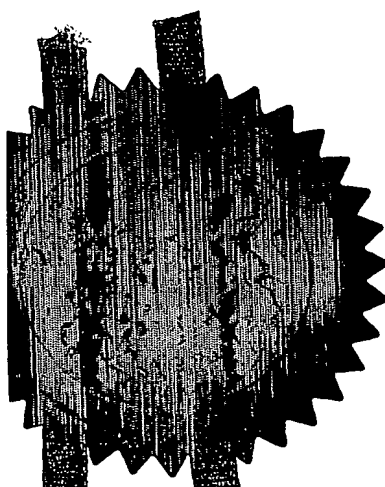
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18 JUL 2003

18 JUL 2003 E823609-4 D02744
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1. Your reference

SMC 60604/GB/P1

2. Patent application number

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom

Patents ADP number (if you know it)

07764137001 ✓

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

Inks and Processes

5. Name of your agent (if you have one)

MORPETH, Fraser Forrest

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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United Kingdom

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Number of earlier application

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Signature C. Shepherd Date 17/1/03
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APPLICANTS

AVECIA LIMITED

TITLE

INKS AND PROCESSES

INKS AND PROCESSES

This invention relates to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

5 Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate. The set of inks used in this technique typically comprise yellow, magenta, cyan and black inks.

10 With the advent of high-resolution digital cameras and ink-jet printers it is becoming increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides a print quickly without the need to post a film to a developing service and wait days or weeks for it to be developed and returned.

15 While ink-jet printers have many advantages over other forms of printing and image development there are still technical challenges to be addressed. For example, there are the contradictory requirements of providing ink-colorants which are soluble in the ink medium and yet do not run or smudge excessively when printed on paper. The inks need to dry quickly to avoid sheets sticking together after they have been printed, but they should not form a crust over the tiny nozzle used in the printer. Storage stability is important to avoid particle formation that could block the tiny nozzles used in the printer.
20 Furthermore, the resultant images desirably do not fade rapidly on exposure to light or common atmospheric oxidising gases such as ozone.

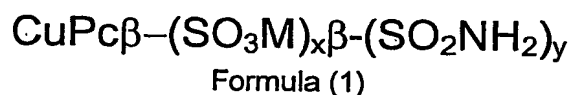
For a number of years C.I. Direct Blue 199 has been used as a colorant for cyan inks used in ink-jet printing. While this colorant has many properties which make it suitable for use in ink-jet printing, prints of C.I. Direct Blue 199 tend to fade and change
25 shade on long term exposure to light and trace oxidising gases present in the atmosphere, such as ozone. The problems of fading and shade change on contact with ozone are particularly acute when phthalocyanine colorants, such as C.I. Direct Blue 199, are printed onto media containing inorganic particles such as silica and/or alumina. There appears to be some aspect of the environment on the surface of such media (particularly media
30 used for photo-realistic ink-jet printing) which promotes deterioration of phthalocyanine dyes in the presence of ozone.

C.I. Direct Blue 199 is copper phthalocyanine carrying sulfo and sulfonamide substituents. C.I. Direct Blue 199 is usually made by sulfonating copper phthalocyanine pigment, chlorinating the sulfonated phthalocyanine and then treating with ammonia to
35 yield a polydisperse product which contains multiple species of phthalocyanines with differing levels of sulfo and sulfonamide substituents where the substituents are present in all susceptible positions on the phthalocyanine ring system.

We have surprisingly found that when C.I. Direct Blue 199 bears substituents only in the β -position of the phthalocyanine ring it yields prints with superior fade properties, especially an enhanced ozone fastness.

Thus, the present invention provides a composition comprising:

- 5 (a) a mixture of copper phthalocyanine dyes of Formula (1):



10 wherein:

CuPc is copper phthalocyanine;

M is a cation;

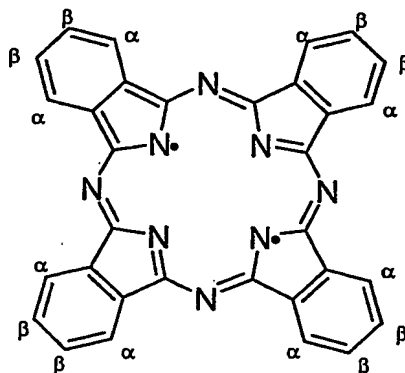
x and y each independently have an average value of from 0.5 to 3.5;

(x+y) = 4; and

15 the sulfo and sulfonamide substituents are attached to a β -position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

20 The phthalocyanine nucleus may be represented by the bivalent radical of formula:



25 When C.I. Direct Blue 199 is made by the more usual route of sulfonating a phthalocyanine pigment followed by chlorination and then amination the resultant product carries sulfo and sulfonamide substituents in any susceptible position.

30 The copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β -position on the phthalocyanine ring may be prepared by any method known in the art, and particularly by cyclisation of appropriate β -substituted phthalic acid, phthalonitrile, iminoisoindoline, phthalic anhydride, phthalimide or phthalamide in the presence of a suitable copper salt, such as CuCl_2 , followed by chlorination and then amination.

Preferably copper phthalocyanine dyes of Formula (1) where the sulfo and sulfonamide substituents are attached to a β -position on the phthalocyanine ring are prepared by cyclisation of 4-sulfo-phthalic acid to phthalocyanine β tetrasulfonic acid in the presence of a suitable copper salt, such as CuCl_2 , followed by chlorination and then amination.

The ratio of sulfo to sulfonamide substituents may be varied by varying the nature and amount of chlorinating agent used, the amount of ammonia added in the amination step and the reaction conditions in both reactions.

When phthalocyanine β tetrasulfonic acid is an intermediate in a route to compounds of Formula (1) it may be chlorinated by reacting with any suitable chlorinating agent.

Chlorination may be carried out by treating the phthalocyanine β tetrasulfonic acid with chlorosulfonic acid preferably in the presence of an acid halide such as thionyl chloride, sulfuryl chloride, phosphorous pentachloride, phosphorous oxychloride or phosphorous trichloride.

The amount of ammonia required to form a compound of Formula (1) will depend to some extent on the composition of and amount of chlorosulfonating agent used. If a large excess of chlorosulfonating agent is used then more ammonia is needed. Thus, the amount of ammonia used is preferably sufficient to bring the pH of the product of the initial chlorination to a pH of 7 to 11, more preferably a pH of 8 to 10.

Preferably the condensation with ammonia to form a compound of Formula (1) is performed at a temperature of 0 to 50°C, more preferably 10 to 45°C and especially 12 to 40°C.

The length of time for which the condensation with ammonia is performed will also depend on the temperature of the reaction. In a preferred embodiment the reaction with ammonia is performed at a temperature of 0 to 45°C for a time of 0.5 to 24 hours.

Preferably x has a value of 1 to 3.

Preferably y has a value of 1 to 3.

The cation represented by M is preferably an alkali metal salt, especially lithium, sodium and potassium, ammonium or a substituted ammonium salt (including a quaternary ammonium salt such as $((\text{CH}_3)_4\text{N}^+)$ or a mixture thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines or mixtures thereof, more especially sodium salts.

When the preferred route, as set out above, is used to synthesise compounds of Formula (1) M is largely ammonium cations. However, any known techniques may be used to exchange the ammonium cation for another cation, for example acidification (e.g. using hydrochloric acid to give $\text{M}=\text{H}$), optionally followed by dialysis, to remove the original cations, with subsequent addition of alternative cations M (e.g. by addition of alkali metal hydroxide, ammonium salt or amine). Use of ion exchange resins and reverse osmosis are other techniques which can be used to exchange one cation for another.

The compounds described herein may exist in tautomeric forms other than those shown in this specification. These tautomers are also included within the scope of the present inventions.

When the medium (b) comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulfolane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example,

aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH_2Cl_2 ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent then preferably a polar solvent is preferably included since this enhances solubility of the compound of Formula (1) in the liquid medium. Examples of polar solvents include C_{1-4} -alcohols.

In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C_{1-4} -alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I. Direct Yellow 86, 132, 142 and 173; C.I. Direct Blue 307; C.I. Food Black 2; C.I. Direct Black 168 and 195; C.I. Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International.

It is preferred that the composition according to the invention is an ink suitable for use in an ink-jet printer. An ink suitable for use in an ink-jet printer is an ink which is able to repeatedly fire through an ink-jet printing head without causing blockage of the fine nozzles.

The inks may be incorporated in an ink-jet printer as a high concentration cyan ink, a low concentration cyan ink or both a high concentration and a low concentration ink. In the latter case this can lead to improvements in the resolution and quality of printed images. Thus the present invention also provides a composition (preferably an ink) where component (a) is present in an amount of 2.5 to 7 parts, more preferably 2.5 to 5 parts (a high concentration ink) or component (a) is present in an amount of 0.5 to 2.4 parts, more preferably 0.5 to 1.5 parts (a low concentration ink).

An ink suitable for use in an ink-jet printer preferably has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C.

An ink suitable for use in an ink-jet printer preferably contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a colorant of Formula (1) or any other component of the ink).

5 Preferably an ink suitable for use in an ink-jet printer has been filtered through a filter having a mean pore size below $10\mu\text{m}$, more preferably below $3\mu\text{m}$, especially below $2\mu\text{m}$, more especially below $1\mu\text{m}$. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

10 Preferably an ink suitable for use in an ink-jet printer contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

Preferred compositions comprise:

(a) from 0.01 to 30 parts of compounds of Formula (1); and

15 (b) from 70 to 99.99 parts of a liquid medium which comprises water and an organic solvent or an organic solvent free from water;
wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

20 Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

25 Compositions according to the present invention yield prints that display a good fastness to water and light. In particular, prints prepared using these inks display excellent light and ozone fastness.

A second aspect of the invention provides a process for forming an image on a substrate comprising applying an ink according to the first aspect of the invention thereto by means of an ink-jet printer.

30 The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an
35 electromechanical actuator connected to a moveable paddle or plunger, for example as

described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

5 Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Glossy papers are especially preferred.

10 A third aspect of the present invention provides a material preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with a composition according to the first aspect of the invention or by means of a process according to the second aspect of the invention.

It is especially preferred that the printed material of the third aspect of the invention is a photograph printed using an ink-jet printer.

15 A fourth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the first aspect of the present invention. The cartridge may contain a high concentration ink and a low concentration ink, as described in the first aspect of the invention, in different chambers.

20 A fifth aspect of the present invention provides an ink-jet printer comprising a cartridge as defined in the fourth aspect of the present invention

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

Step 1

Preparation of a compound of Formula (1) where x is 2, 3 and y is 1.6:

Analysis of compounds of Formula (1)

30 Conformation of the structure of compounds of Formula (1) is by mass spec. Elemental analysis is used to determine the ratios of x to y. When the sum of x plus y is not exactly 4 this is due to the presence of small amounts of impurity. The presence of these impurities and their effect on the estimated values of x and y would be well known to a person skilled in the art who would appreciate that the value of x plus y will not exceed 4 and who would treat the experimentally determined values of x and y as indicative of the
35 true ratios of the two groups. .

Stage 1 - Preparation of copper phthalocyanine substituted with 4-SO₃H groups in the β position

40 Potassium 4-sulfophthalic acid (56.8g), urea (120g), CuCl₂ (6.9g), ammonium molybdate (1.2g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (7.5g) were mixed in a

reaction vessel. The mixture was then warmed in stages (130°C/30 minutes, 150°C/30 minutes, 180°C/30 minutes, 220°C) over 2 hours and the melt which formed was stirred at 220°C for a further 2 hours. The solid that formed was extracted 4 times with hot water (4 x 200ml) and the extract was filtered to remove insoluble material. The resultant filtrate was stirred at between 60°C – 70°C and then sufficient NaCl was added to give a 7% salt solution. Stirring was continued and the solid that precipitated was filtered, washed with a 10% salt solution (200 ml) and pulled dry by vacuum. The resultant damp solid (77.6g) was slurried in acetone, filtered and dried first at room temperature and then at 50°C.

Stage 2 - Preparation of the title product

Stage 2 (a) Preparation of phthalocyanine sulfonyl chloride:

Phosphorous oxychloride (1.65g) was added to chlorosulfonic acid (27.1g) at 28°C. The sulfonated phthalocyanine product of stage 1 (9.8g) was then added to this mixture over 10-15 minutes while keeping temperature below 60°C. This reaction mixture was stirred at 50°C for 15-20 minutes and then slowly warmed to 120°C – 125°C and kept at this temperature, with stirring for 3 hours. At the end of this time the reaction mixture was cooled and stirred at room temperature overnight. The next day the reaction-melt was added to a mixture of water/ice/salt/HCl (50ml/150g/10g/2.5ml), keeping the temperature below 0°C using external cooling and further addition of ice as necessary. The resultant suspension was stirred at 0°C for 30 minutes and then filtered, washed with an acidified ice cold 10% salt solution (100 ml) and pulled dry by vacuum to give 30g of the product as a damp paste.

Stage 2 (b) Amidation of phthalocyanine sulfonyl chloride to give the title product

The phthalocyanine sulfonyl chloride paste from stage 2(a) was added portion-wise to a 150 ml of a cold aqueous solution of ammonium chloride (0.8g) and stirred at 0°C to 5°C for 15-20 minutes. The pH of the mixture was slowly adjusted to 9.5 with 2 M NaOH solution and stirred at 0°C to 5°C for a further 30 minutes. The mixture was then left stirring overnight at room temperature. The next day the reaction mixture was warmed to 70°C to 80°C and stirred for 2 hours while maintaining the pH at pH 9.5 by the addition of 2M NaOH solution. The reaction mixture was then filtered and the filtrate (350 ml) was adjusted to pH 6-7 and NaCl was added in stages to give a 20% salt solution which was stirred at 60°C. The precipitated solid which formed was filtered, washed with a 20% salt solution and pulled dry by vacuum to give 23.5g of a damp paste. This paste was re-dissolved in deionised water (150 ml) at pH 8.5 and dialysed to a low conductivity. The product was then filtered and dried at 50°C to 60°C to give a final yield of 7.5g.

Step 2Preparation of the ink:

An ink of the present invention may be prepared by dissolving 3.5g of the dye prepared in step 1 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Example 2Step 1Preparation of the title product where x is 0.8 and y is 3.1Stage 1

Stage 1 was carried out as in Example 1.

Stage 2 (a) Preparation of phthalocyanine sulfonyl chloride:

Concentrated sulfuric acid (0.6ml, density 1.84) was added to chlorosulfonic acid (18.3 ml, 32.3 g) with stirring at room temperature. The sulfonated phthalocyanine product of stage 1 was added portion-wise to the acid mixture over 15 to 20 minutes. The resultant reaction mixture was stirred at 40° to 50°C for 15-20 minutes and then 112° to 113°C for 6 hours. The mixture was allowed to cool to room temperature overnight and then added to a mixture of water/salt/concHCl/ice (50g/7.5g/3ml/120g) while keeping the temperature below 0°C using external cooling and further addition of ice as necessary. The resultant suspension was stirred at 0°C for 30 minutes and then filtered, washed with an ice cold acidified 10% salt solution (50 ml) and pulled dry by vacuum to give the product as a damp paste.

Stage 2 (b) Amidation of phthalocyanine sulfonyl chloride to give the title product

The phthalocyanine sulfonyl chloride paste from stage 2(a) was added portion-wise to a mixture of water/ice/concentrated ammonia solution (90ml/15g/10ml) and stirred at 0°C to 5°C for 15-20 minutes. The pH of the mixture was slowly adjusted to 9.5 with 2 M NaOH solution and stirred at 0°C to 5°C and a pH greater than 10 for 2 hours and then left stirring overnight at room temperature. The mixture was then heated up to room temperature and the reaction mixture was left stirring overnight. The next day the reaction mixture was heated to 40°C and stirred at a pH greater than 9 for 2 hours. The temperature was then increased to 70° - 72°C and the mixture was stirred for a further 30 minutes. The pH of the mixture was adjusted to 1.0 with concentrated HCl and NaCl was added to give a 20% salt solution. The mixture was then stirred and the precipitate which formed was filtered, pulled dry by vacuum and dried at 50°C to give 9.2 g of product.

Step 2Preparation of the ink:

An ink of the present invention may be prepared by dissolving 3.5g of the dye prepared in step 1 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Example 1 and 2. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na₂HPO₄ and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE A

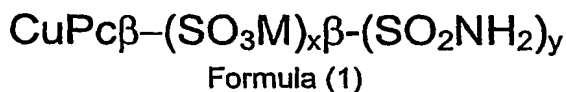
Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2			5	1	
1	10.0	85	3		3							1
2	2.1	91		8				0.2	4			5
1	3.1	86	5				0.5	0.5	6		9	4
2	1.1	81			9				10	10	5	
1	2.5	60	4	15	3	3						
2	5	65		20						6		5
1	2.4	75	5	4		5		0.3				
2	4.1	80	3	5	2	10			5	4	6	5
1	3.2	65		5	4	6				4		
2	5.1	96							5			
1	10.8	90	5						1		4	
2	10.0	80	2	6	2	5					15	
1	1.8	80		5							5	
2	2.6	84			11					2		6
1	3.3	80	2			10			3			
2	12.0	90				7	0.3				3	3
1	5.4	69	2	20	2	1					5	
2	6.0	91			4							

TABLE B

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
1	1.5	85	5	5		0.15	5.0	0.2		0.12		
2	2.5	90		6	4							6
1	3.1	82	4	8		0.3						
2	0.9	85		10					5	0.2		
1	8.0	90		5	5			0.3				
2	4.0	70		10	4				1		4	11
1	2.2	75	4	10	3				2		6	
2	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
2	5.0	78	5	11							6	
1	5.4	86			7						7	
2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
1	2.0	90		10								
2	2	88						10				
1	5	78			5			12			5	
2	8	70	2		8			15			5	
1	10	80						8			12	
2	10	80		10								

CLAIMS

1. A composition comprising:
(a) a mixture of copper phthalocyanine dyes of Formula (1):



wherein:

- CuPc is copper phthalocyanine;
M is a cation;
x and y each independently have an average value of from 0.5 to 3.5;
(x+y) = 4; and
the sulfo and sulfonamide substituents are attached to a β -position on the phthalocyanine ring; and
(b) a medium which comprises water and an organic solvent or an organic solvent free from water.

2. A composition according to claim 1 wherein the copper phthalocyanine dyes of Formula (1) are prepared by cyclisation of 4-sulfo-phthalic acid to phthalocyanine β tetrasulfonic acid in the presence of a suitable copper salt followed by chlorination and then amination.

3. A composition according to either claim 1 or claim 2 where in the copper phthalocyanine dyes of Formula (1) x is 1 to 3.

4. A composition according to any one of the preceding claims where in the copper phthalocyanine dyes of Formula (1) y is 1 to 3.

5. A composition according to any one of the preceding claims where M is sodium, lithium, ammonia and volatile amines or mixtures thereof.

6. A composition according to any one of the preceding claims which comprises:
(a) from 0.01 to 30 parts of compounds of Formula (1); and
(b) from 70 to 99.99 parts of a liquid medium which comprises water and an organic solvent or an organic solvent free from water;
wherein all parts are by weight and the number of parts of (a)+(b)=100.

7. A composition according to any one of the preceding claims which is an ink suitable for use in an ink-jet printer.

8. A process for forming an image on a substrate comprising applying an ink according to claim 7 thereto by means of an ink-jet printer.

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9. A material printed with a composition according to any one of claims 1 to 7 or by means of a process according to claim 8.

10. A material according to claim 9 that is a photograph printed using an ink-jet printer.

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11. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in claim 7.

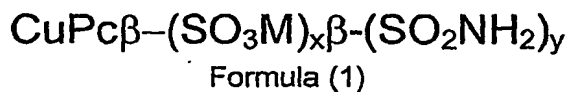
12. An ink-jet printer comprising a cartridge as defined in claim 11.

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ABSTRACT
INKS AND PROCESSES

A composition comprising:

- 5 (a) a mixture of copper phthalocyanine dyes of Formula (1):



- 10 wherein:

CuPc is copper phthalocyanine;

M is a cation;

x and y each independently have an average value of from 0.5 to 3.5;

(x+y) = 4; and

- 15 the sulfo and sulfonamide substituents are attached to a β -position on the phthalocyanine ring; and

(b) a medium which comprises water and an organic solvent or an organic solvent free from water. Also ink-jet printing processes, printed images, printers and cartridges.

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